DYE REMOVAL BY THIN FILM COMPOSITE (TFC) MEMBRANE PRODUCED THROUGH INTERFACIAL POLYMERIZATION TECHNIQUE

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ABSTRAK

Terdapat banyak jenis teknik penyingkiran pewarna seperti kaedah biologi, kaedah kimia, dan kaedah fizikal. Membran – penapisan adalah salah satu kaedah fizikal yang meluas digunakan untuk penyingkiran pewarna. Membran komposit filem nipis disintesis melalui pempolimeran antaramuka pada kepekatan monomer 2% dan reaksi masa yang berbeza. Tindak balas antara larutan triethanolamine (TEOA) dan trimesoylchloride (TMC) dalam heksana menghasilkan lapisan baru poliester di atas miroporous sokongan polyethersulfone (PES). Membran filem nipis komposit yang dihasilkan dicirikan dari segi fluks dan ketelapan. Di samping itu, prestasi membrane telah diuji untuk penyingkiran pewarna menggunakan metilena biru sebagai model pewarna. Meningkatkan masa tindak balas menyebabkan mengurangkan kebolehtelapan air dan meningkatkan kecekapan penyingkiran.

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LIST OF SYMBOLS

Cp	Concentration of permeate
Cf	Concentration of feed
h	Hour
P	Permeability
b	bar
J	Permeate flux
L	Liter
M	Meter
ΔP	Filtration pressure
R	Rejection
Δt	Filtration time
V	Volume

LIST OF ABBREVIATIONS

TEOA	Triethanolamine
TMC	Trimesoylchloride
PES	Polyethersulfone
PVP	Polyvinylpyrrolidone
NMP	N-metyl-pyrrolidone
MB	Methylene Blue
UF	Ultrafiltration
RO	Reverse Osmosis
NF	Nanofiltration
IF	Interfacial Polymerization

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Textile industries generally produced dye wastewater which generates from dyeing, printing, and other process of coloring in its daily operation. Facts shows, the dye wastewater contains many dangerous chemical such as dyes, detergents sulphide compound, solvents, heavy metals and other dangerous substances. Therefore, dye wastewater cannot directly discharged from the factory because it has striking effect on receiving water body which sooner or later can cause harm to the environment, aquatic life and especially human. Many textile industries out there use a huge amount of water to decrease the pollution load from discharged wastewater. That practice increase the textile industries operation cost just for water consumption. So, it is better if textile industries use one type of treatment system which profitable operation through recycling the dye wastewater and at the same time protecting the environment (Lau and Ismail, 2009). That treatment system is called Nanofiltration. This treatment system allow for recovery of water and valuable chemical compound from dye wastewater.

Nanofiltration membrane separation are widely use in various industrial fields. Wastewater treatment is one of the field that use this kind of technology to treat the water until the water reach the quality that it can be discharged to the environment or reusable for other process. Nanofiltration has been knew having the properties in between reverse osmosis and ultrafiltration (Mansourpanah *et. al*. 2010). Because of that, it has significant advantages including low operation pressure, higher permeation flux, high retention of multivalent salt, molecular weight compound more than 300, and low investments, operation and maintenance costs (Tang *et al.* 2008). Nanofiltration membrane are produced by using two preparation steps which is polymer phase inversion resulting a microporous support membrane and interfacial polymerization of a thin film composite (TFC) layer on top of a miroporous support membrane or other porous substrate (Mohammad *et al.* 2003).

The thin film composite layer can be prepared using interfacial polymerization. Thin-film composite membranes are usually studied in reverse osmosis and nano-filtration. The interfacial polymerization has significant advantages which involve rapid reaction rates under ambient conditions, no requirement for reactant stoichiometric balance and a low requirement for reactant purity (Li *et al.* 2008). The interfacial polymerization technique is an adequate method for the preparation of composite membranes with an ultra thin polyester active layer. In this study, thin-film polyester composite membranes were prepared using interfacial polymerization for dye removal.

1.2 PROBLEM STATEMENT

Dyes is one of the substance contain in textile wastewater. Dyes are considered as problematic because the families of chemical compounds that make good dyes are also toxic to humans. Each new synthetic dye developed is a brand new compound, and because it's new, no-one knows its risks to humans and the environment. Therefore, because of these reasons, dye from textile industrial wastewater need to be removed.

In this research, nanofiltration membrane process is used because of its advantages. The major advantages of nanofiltration are

- No chemical additive
- Removal for health-related contaminants
- Removal of suspended solids, some dissolve ions, and other non-health related contaminant.
- Cost effective and low maintenances costs.

Retrieved from (Nanofiltration article by Peter S. Cartwright)

`The chosen thin film composite membrane is polyester membrane which is considered new in the field of composite thin-film membrane development compared to polyamide for example. In addition, the future nanofiltration in textile industries is also provided in view of developing a more competitive nanofiltration membrane, especially for textile wastewater treatment.

1.3 RESEARCH OBJECTIVES

The objective of this experiment is to produce Nanofiltration Polyester membrane for dye removal.

1.4 SCOPES OF STUDY

In order to achieve the objective of this research, the scope of study has been determined based on two parameters to produce polyester. These are including effect of monomer concentration and reaction time on membrane performance.

1.5 SIGNIFICANCE OF STUDY

This research purpose is to prepare the NF membrane which suitable for dyes removing from textile industries. If the dyes completely can be removed by this filtration method, the wastewater discharged volume could be minimized and thus reducing impact on environment.

CHAPTER 2

LITERATURE REVIEW

This chapter will describe detail about the basic concepts of membrane separation technology, background of the membrane, type of membrane which will be use in the experiment (nanofiltration membrane) and also information about dyes and the technologies of dye removal. It will cover it characteristic, and the filtration mechanism.

2.1 MEMBRANE REVIEW

Membrane has been used in various fields such as waste treatment, medical purpose and many more. The selective permeability characteristic of membrane made it very useful especially in filtration and separation process.

2.1.1 Membrane Definition

The word membrane originally comes from the Latin word "*membrane*" which means skin. The other definition of membrane are a thin barrier that permits selective mass transport, selective barrier between two phases, and a phase that acts as a barrier to prevent mass movement, but allows restricted and / or regulated passage of one or more species (Wang *et. al.* 2011).

2.1.2 Membrane Separation Process

Membrane is a thin layer which allows smaller molecule liquid or gas than its pore size to pass through it. These pores size normally measured in Armstrong scale or micron. The thickness of the membrane usually is between 100 nm until a few centimeters over. The membrane layer is supported by a supported layer which is strong and thick. These limited routes of membrane only allow selected liquid or gas which means the other particle could not get into this membrane. The separation through membrane is effected by absorption, convection, concentration, pressure, the charge value of the solution, operation time and the temperature (Hesampour, 2009).

Membrane uses separation process as it operation. The basic membrane separation is shown in Figure 2.1

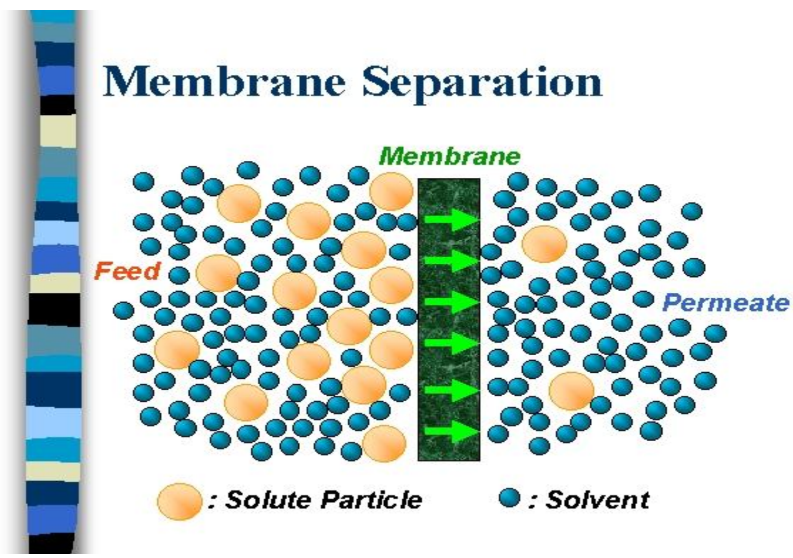

Figure 2.1: Basic Membrane Separation Process

Retrieved from (http://www.yale.edu/env/elimelech/Conc-Polarization/sld002.htm)

2.2 DRIVING FORCE OF MEMBRANE PROCESS

Based on the main driving force, which is applied to accomplish the separation, many membrane processes can be distinguished. An overview of the driving forces and the related membrane separation processes is given in Table 1.1

Table 2.1: Driving forces and their related membrane separation processes

Driving Force	Membrane Process
Pressure Differences	Microfiltration, ultrafiltration, nanofiltration, reverse osmosis or hyperfiltration
Chemical potential differences	Pervaporation, pertraction, dialysis, gas separation, vapor permeation, liquid membranes
Electrical potential differences	Electrodialysis, membrane electrophoresis, membrane electrolysis
Temperature differences	Membrane distillation

Source adapted from (Timmer, 2001)

Each membrane processes have their own mechanism and applications. For example, pressure driven membrane separation processes, electrodialysis and gas separation are industrially implemented and are generally considered as proven technology (Timmer, 2001).

2.2.1 Pressure Driven Membrane

Four pressures driven membranes are distinguished in practice (Timmer, 2001)

1. Microfiltration (MF), which is characterized by a membrane pore size between 0.05 and 2 µm and operating pressures below 2 bars. MF is primarily used to separate particles and bacteria from other smaller solutes.

2. Ultrafiltration (UF), this is characterized by a membrane pore size between 2 nm and 0.05 µm and operating pressures between 1 and 10 bars. UF is used to separate colloids like proteins from small molecules like sugars and salts.

3. Nanofiltration (NF),this is characterized by a membrane pore size between 0.5 and 2 nm and operating pressures between 5 and 40 bars. NF is used to achieve separation between sugars, other organic molecules and multivalent salt on one hand and monovalent salts, ions and water on the other.

4. Reverse osmosis (RO) or hyper filtration, which is characterized by a membrane pore size in the range of 0.0005 microns. Some researchers consider the RO membrane as without have pores. Transport of the solvent is accomplished through the free volume between the segments of the polymer of which the membrane is constituted. The operating pressures in RO are generally between 7 and 100 bar and this technique is mainly used to remove water.

Membrane Application can be seen in Table 1.2

Table 2.2: Membrane Applications

Process	**Advantages**
Microfiltration	Sterile solution, water purification, baverage filtrationeffluents
Ultrafiltration	Protein concentration(enzyme), oily wastewaters effluent, blood fractionation, antibiotic separation
Nanofiltration	Potable water, desalination of brackish water, polyvalent ions stream cleaning, whey fractionation
Reverse Osmosis	Food concentration, water purification, desalination (monovalent ions stream), biomedical application
Electrodialysis	Desalination, water purification, deacidification of citrus juice.
Gas permeation	Separation of He from natural gas, He recovery, CO2 removal, NG dehydration
Pervaporition	Dehydration of organic solvents

Source adapted from (Muhsen, 2011)

2.2.2 Advantages of Membrane Processes

Compared with the conventional methods, membrane systems offer more economical benefits over conventional systems. The followings are specific criteria of the membrane system (Mustaffar, 2004):

1. Flexibility and versatility; as this technology can be applied at wide spectrum of separation ranges comparable to conventional methods. The system can be operated in combination with the conventional methods and /or on its own.

2. Simplicity of operation; that is the system is relatively less complex and less sophisticated.

3. Low energy consumption; membrane systems consume less energy since separation does not involve phase change. Thus the system driving force is mainly pressure provided by using pump.

4. Low capital and maintenance cost; the overall membrane system is (30-40) % cheaper than the corresponding conventional systems.

5. Reliability; the membrane system is very reliable and requires minimum human intervention during operation.

6. Physical separation; separation is done physically thereby undesirable by products and no side reactions, no waste generation and is environmentally green.

2.3 NANOFILTRATION MEMBRANE

Nanofiltration membrane is classified as anisotropic membranes. Anisotropic membrane are non-uniform over cross-section and they typically consist of layers which vary is structure and/or chemical composition. There are two main types of anisotropic membrane which is phase separation membranes and thin film composite membranes. Phase separation membranes are homogeneous in chemical composition but not in structure and often consist of a rather dense layer of polymer on the surface of an increasingly porous layer. This membrane is produced via phase inversion. While thin film composite membranes are both chemically and structurally heterogeneous. Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. This membrane can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment.

2.3.1 The Asymmetry

The Nanofitration membrane is asymmetry membrane. It will not allow the larger molecule to pass through the membrane and will stop at the surface. While the smaller molecule will pass through the membrane and known as permeate.

2.3.2 Pore Size

There are many types of membrane use in industry and one of them is nanofiltration. The nominal pore size for this type of membrane is between 0.5 and 2 nanometer.

2.3.3 Mass Transfer in Nanofiltration

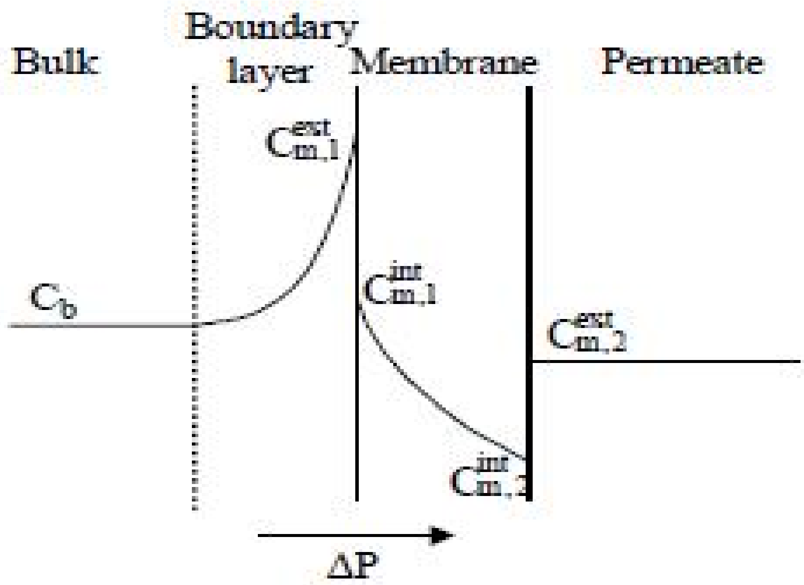

Figure 2.2: Mass transfer in nanofiltration

When an external pressure *ΔP* is imposed on a liquid which is adjacent to a semi-permeablemembrane, solvent will flow through the membrane. The general terms that are used in thedescription of membrane separation processes are the solvent flux (J) and the rejection (R). Thesolvent flux is given by Eq. 2.1

$$J = \frac{W}{A\Delta t} \qquad (2.1)$$

Where W is the weight of the obtained permeateduring a predeterminded Nanofiltration operation time Δt and A is the membrane area.

A neutral solute dissolved in the solvent at a concentration level Cf will also flow towards the membrane. If the membrane exhibits rejection for the solute, partial permeation will occur andnon-permeated solute accumulates in the boundary layer, and hence a concentration profiledevelops. This phenomenon is called concentration polarisation. The solute distributes at the membrane/solution interface and will be transported through the membrane by convection and diffusion. At the permeate side, a second distribution process will occur and a final concentrationof solute in the permeate, *Cp* will be reached. Rejection as Eq. 2.2

$$R = \left(1 - \frac{Cp}{Cf}\right) x\ 100 \qquad (2.2)$$

The membrane permeance, *Pm* can be determined from the slope obtained by plotting the permeate flux *J* against ΔP :

$$Pm = \frac{J}{\Delta P} \qquad (2.3)$$

2.4 THIN FILM COMPOSITE MEMBRANE

Thin film composite the top layer is formed by a variety of techniques ranging from simple solution casting such as spin coating to intricate polymerizations like interfacial polymerization, in-situ polymerization, plasma polymerization and grafting (Dalwani, 2011).

2.4.1 Spin Coating

Spin coating is quick and easy laboratory method to produce thin film composite. This technique use centrifugal force mechanism. An excess of solution is pour on the ultraporous substrate that is then rotated at high speed. A uniform layer will form on substrate when liquid spreads due to the centrifugal forces. Evaporation of solvent results a uniform solid polymer coating. The schematic of spin coater is shown as Figure 2.3

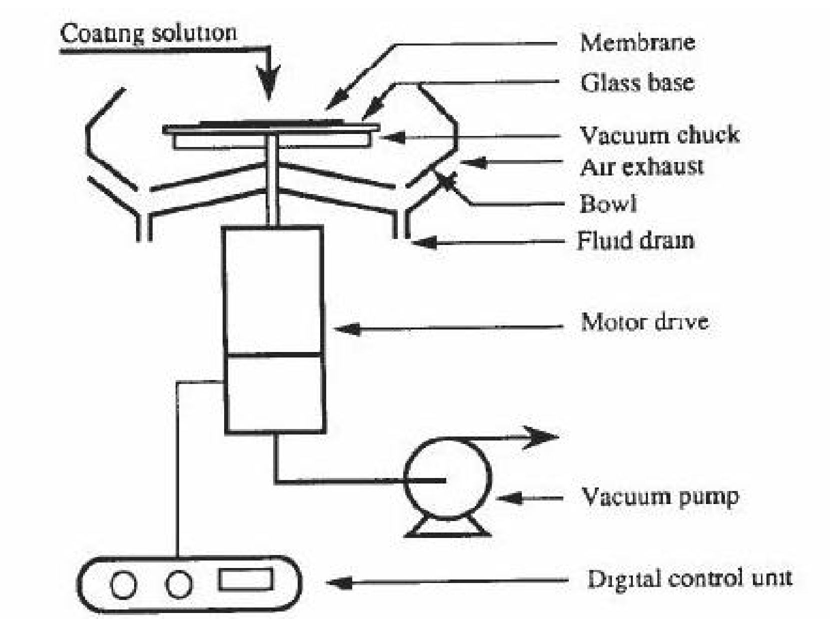

Figure 2.3: Schematic of spin coater

Source adapted from (Dalwani, 2011)

The quality of the thin coating layer depends mainly on the spinning speed, solvent evaporation rate, viscosity or concentration of the polymer solution and the pore and surface characteristics of the support. Spin coating has limited application in the field of membrane technology on a commercial scale, due to restricted product size, but benefits from the minimal amount of required polymer solution.

2.4.2 Interfacial Polymerization

The thin film composite was produced via polymerization which takes place at the interface of the two liquids which are insoluble to each other (Lau *et.al* 2011). It is carried out between two highly reactive monomers dissolved in two immiscible solvents (Dalwani, 2011). Even though the interfacial polymerization (IP) involves many complex parameters compared to spin coating, it is the major technique to produce commercial TFC membranes because composite membranes with surprisingly high flux could be made by interfacial crosslinking. The IP process consists of a sequence of steps, as shown in Figure 2.4. In the first step an ultraporous support is pretreated to make it suitable for the IP process. In the second step, the substrate is immersed in aqueous solution containing one of the monomer. Then, continue immersed in second solution containing the second monomer. Since the two solutions in immiscible to each other, the interface is created between them. One of the monomer travels through the interface and react with the other polymer to produce polymerized product. IP layer usually dense and very thin due to high reactivity of two monomers and limited barrier created at interface.

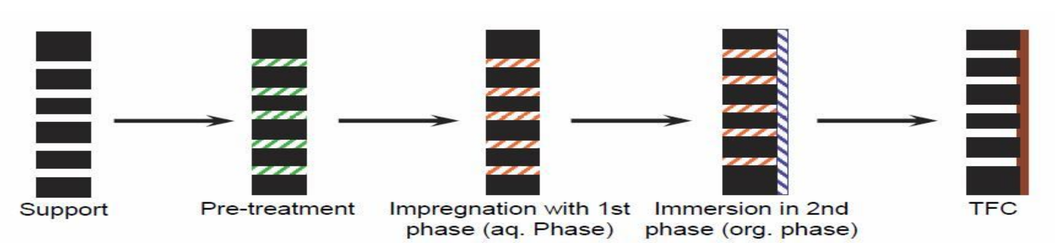

Figure 2.4: Interfacial Polymerization Process

Source adapted from (Dalwani, 2011)

In order to produce a variety type with high performance of membrane, there are several parameters which can be varied during IP process which is

1. Different monomer types – Many types of monomer can be used in both aqueous and organic phase. Piperazine is an example of monomer used to make NF membrane as aqueous phase reactant and types of acyl chloride such as trimes

2. Monomer concentration and reaction time – In general high monomer concentration, high reaction rates, longer polymerization time results in thicker layers with high rejection but lower flux.

2.4.3 Triethanolamine (TEOA) as Monomer

There is only few research that use TEOA as monomer as well as to produce polyester composite membrane which considered new because most of the research for the composite membranes are more to the production of polyamide. Compare to other monomer like Bisphenol A which also used to produce polyester membrane, TEOA is less dangerous to human health. Then, it is natural to seek an inexpensive monomer to manufacture a new membrane. It is found that triethanolamine (TEOA) is an active monomer which is environment-friendly, economical and easy to be obtained (Tang *et. al*, 2008).